RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 36, NUMBER 7 OCTOBER 1, 1987

Precise two-photon spectroscopy of $E \leftarrow X^*$ intervals in H_2

E. E. Eyler, J. Gilligan, E. McCormack, A. Nussenzweig, and E. Pollack*
Department of Physics, Yale University, New Haven, Connecticut 06511

(Received 8 June 1987)

We have precisely measured the vacuum ultraviolet intervals between several rotationally and vibrationally excited levels of ground-state H_2 and the $E,F\,{}^1\Sigma_g^+$ state. An accuracy of 0.01 cm^{-1}, an order of magnitude better than previously available, is achieved using a pulsed discharge source in conjunction with a pulse amplified cw laser system. These measurements also serve as a calibration for numerous other excited states connected by optical intervals to the E,F state.

The properties of the $X(1s\sigma)\,{}^1\Sigma_g^+$ ground state of H_2 are among the most fundamental quantities in molecular physics. These include the dissociation energy, the ionization potential, and the vibrational and rotational energy intervals. *Ab initio* calculations of these properties have been carried out with remarkable accuracy, exceeding that of the best current measurements. It is experimentally very difficult to measure any of these quantities because vibrational and rotational transitions within the ground state are nearly impossible to observe, and a large energy gap separates it from all electronically excited states. Only for the lowest few vibrational and rotational levels have precise infrared intervals been measured.[1] For larger intervals, and to determine the vibrational and electronic binding energies, it is necessary to measure precisely transitions to excited states in the vacuum ultraviolet region.

For this purpose, we have investigated two-photon transitions to the E,F state near 95 000 cm^{-1} to an accuracy of 0.01 cm^{-1}. This is the most accurate vacuum uv spectroscopy so far performed on H_2. The E,F state is of particular interest because it can be used as a convenient intermediate state for stepwise excitation. Its double-well potential curve is shown in Fig. 1. The inner well, the E state, has a singly excited $(1s\sigma)(2s\sigma)$ configuration, while the outer F state well has a $(2p\sigma)^2$ configuration and can be regarded as an ion-pair state. The state has a long lifetime of 100–200 nsec,[3] and the double minimum potential curve covers so wide a range of internuclear separations that vibrational levels can be selected having favorable Franck-Condon factors to nearly any higher excited state.

In the past few years several such stepwise measurements have been made. The E,F state has been used in studies of autoionizing Rydberg *np* states,[4,5] of states near the second dissociation limit,[6] and of the dissociation energy.[7] The $c\,{}^3\Pi_u$ and $5f$ Rydberg states have also served as intermediate states.[8,9] These measurements have determined the dissociation energy and ionization potential to higher accuracy than the pioneering vacuum uv work of Herzberg.[10-12] They are presently slightly less precise than the best theoretical calculations,[13] with an error limited principally by uncertainty in the energy separating the ground state from the lowest excited states.

The best existing measurements of intervals from the ground state are the determination of numerous $B\,{}^1\Sigma_u^+ \leftarrow X$ and $C\,{}^1\Pi_u \leftarrow X$ transitions by Dabrowski using vacuum uv emission and absorption spectroscopy,[14] accurate to 0.1 cm^{-1}, and two-photon measurements of the $E,F,v'=0 \leftarrow X,v''=0$ band by Glab and Hessler (in the present paper the vibrational numbering refers to the E-state well).[5] The specified accuracy of the $E,F \leftarrow X$ measurements is 0.04 cm^{-1}, but they disagree by up to 0.08 cm^{-1} with the results presented here. Preliminary new work by Glab and Hessler suggests that the previous measurements were affected by power-dependent shifts in the stimulated Raman process they used.[15] A few $B \leftarrow X$ and $C \leftarrow X$ transitions have also been studied using high-resolution three-photon spectroscopy; preliminary results agree with Dabrowski and are accurate to about 0.05 cm^{-1}.[16]

The new measurements reported here were made using two-photon resonant, three-photon ionization in a collimated molecular beam. Two very recent developments have made this possible. The first is our development of a simple source that produces an intense beam of vibrationally and rotationally excited ground-state H_2. The second

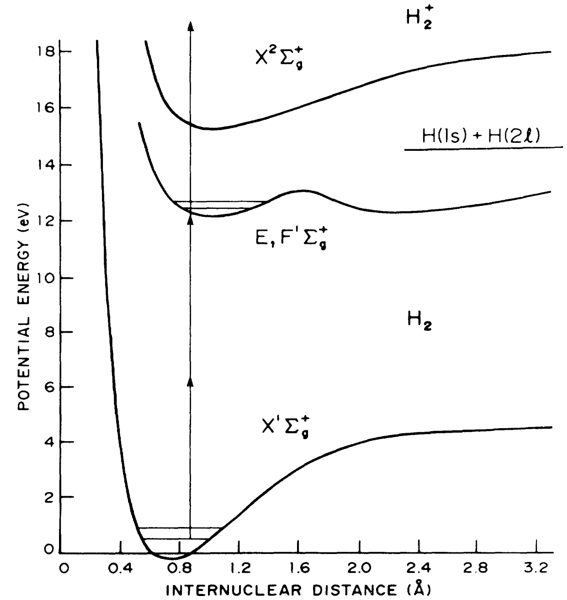

FIG. 1. Excitation and detection scheme. Potential curves are from Ref. 2.

is the availability of a new frequency doubling crystal for laser radiation, β-BaB_2O_4, that is useful down to 204.7 nm.[17] While the range for frequency doubling is not sufficient to access the (0,0) band of the $E,F \leftarrow X$ transition, it encompasses numerous vibrational bands from the $v=1$, 2, and 3 levels of the X state. The energy levels involved in this measurement are shown in Fig. 1.

Intense pulsed laser radiation is derived from the output of a cw ring dye laser by amplifying it with a three-stage excimer pumped pulsed amplifier chain. The amplified pulses are about 10-nsec long, with typical energies of 2–6 mJ. They are frequency doubled into uv pulses with an energy of about 250 μJ and a bandwidth of 0.005 cm^{-1}. The uv light is focused by a 50-cm lens into a spot roughly 50 μm in diameter where it intersects, at right angles, a collimated molecular beam of vibrationally excited H_2.

The molecular beam is formed by an intense, quasistatic discharge in a pulsed supersonic expansion, similar to the arrangement used recently by Johnson to form a metastable N_2 beam.[18] The beam source is a commercial Lasertechnics LPV nozzle producing 100-μsec pulses, and is operated with pure H_2 expanding through a 0.3-mm orifice with a backing pressure of 40 psi (gauge). Two ring-shaped nickel electrodes, 3 mm in diameter, are positioned in the collisional region of the expansion slightly outside the orifice. The one closest to the nozzle faceplate is kept at ground while the other is maintained at a positive potential across a 0.05-μF storage capacitor, in series with a 500-Ω resistor and a 30-kV Krytron trigger (EG&G TR-12). The discharge can be initiated by the trigger or, at higher voltages, will self-initiate when the gas pulse begins. The storage capacitor sustains the discharge for 10–50 μsec. While the mechanism of formation for vibrationally excited H_2 is not fully understood, it is likely that the Shultz resonances observed in low-energy inelastic electron scattering are in large part responsible.[19]

Depending on the parameters of the discharge, both excited ground state and metastable $c(2\pi)\,{}^3\Pi_u$ state H_2 can be produced. Large signals are obtained only when the outer electrode is positive, possibly because the electrons oscillate about the position of the outer electrode when it has this polarity. Signals of order 10^6 ions per laser shot were observed, indicating total production of well over 10^{11} excited molecules per gas pulse in the collimated beam.

After the beam passes through a collimating skimmer plate, a 100-V/cm electric field deflects charged particles. A second skimmer further collimates the beam and, along with simple light baffles, reduces background due to uv photons from the discharge. The laser crosses the molecular beam 21 cm from the nozzle, and a multiplier tube (EMI D233B) mounted vertically about 4 cm above the crossing point detects ions resulting from multiphoton ionization. A gated integrator is used to acquire the $H_2{}^+$ signal, which can easily be distinguished from other ions by its time of flight. This signal is averaged over three laser shots. Reference scans of the absorption spectrum of Te_2 (at 500 °C) and of the fringes from an interferometer with a free spectral range of 2 GHz are recorded to calibrate and linearize the data scans, and the cw laser power is recorded to normalize the reference scans. Data points were acquired at 20-MHz intervals in the scan of the visible dye laser. At least three scans were taken for each transition.

Figure 2 shows a representative spectrum, the $Q(3)$ branch of the (0,2) band. The linewidth of 0.015 cm^{-1} is determined mainly by the residual Doppler width of the molecular beam, collimated by a 60:1 ratio for this scan. We measured 22 intervals in the (0,1), (0,2), and (1,2) bands of $E \leftarrow X$. The results are listed in Table I.

In the (0,2) and (1,2) bands we measured Q branches up to $N=6$ and $N=5$, respectively. A few S branches were also observed. In the (0,1) band we detected Q branches as high as $N=9$. Although no serious attempt was made to measure absolute line strengths, the rotational population distribution in the discharge appears qualitatively to be nonthermal. Even the $Q(9)$ branch of the (0,1) band is quite strong, and it is likely that much higher Q branches can be observed. The intensities of lines in the (0,2) band are roughly an order of magnitude lower than for the (0,1) band. Since the vibrationally averaged transition moments are similar, this can be taken as a crude estimate of the ratio of vibrational populations in the ground state. The (1,2) band is weaker than (0,2) by a factor of 10–20, in agreement with our calculation of the transition moments.

Several sources of random and systematic error were considered. Preliminary line positions were determined by fitting the H_2 and Te_2 lines to Gaussians. Scan nonlinearities were corrected using Lagrange interpolation between the regularly spaced 2-GHz fringes of the reference interferometer. The locations of the Te_2 and H_2 peaks were assigned uncertainties due to the granularity of the data, the time constant associated with averaging the H_2 data, the error due to thermal drift of the reference interferometer, and the uncertainty of the Te_2 transition energies cited in the atlas.

The Te_2 spectrum is quite dense over the experimental Doppler width; the lines we observed often contain several

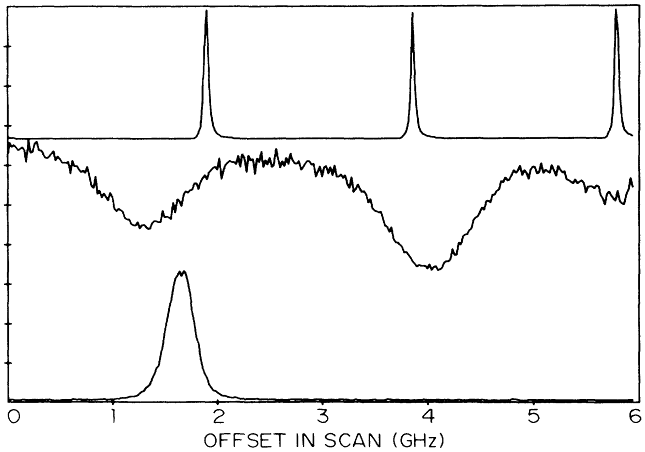

FIG. 2. Lower trace: Scan over the $Q(3)$ branch of the (0,2) band. Middle trace: reference scan of Te_2 absorption; upper trace: frequency markers from interferometer with a free spectral range of 2 GHz.

TABLE I. Transition energies in cm^{-1} for three $E \leftarrow X$ bands.

	(0,1)	(0,2)	(1,2)
$Q(0)$	95003.628(12)	91077.800(10)	93407.744(12)
$Q(1)$	94954.480(10)	91034.436(10)	93360.244(16)
$Q(2)$	94856.728(12)	90948.208(10)	93265.284(10)
$Q(3)$	94711.376(12)	90820.072(10)	93126.704(10)
$Q(4)$	94519.956(12)		92941.136(10)
$Q(5)$	94284.336(12)		92712.960(10)
$Q(6)$	94006.808(10)		
$Q(7)$	93689.848(10)		
$Q(8)$	· · ·		
$Q(9)$	92948.744(16)		
$S(1)$		91348.984(10)	
$S(2)$		91384.980(10)	
$S(3)$		91375.564(10)	

TABLE II. E-state term energies in cm^{-1}.

N	$v=0$	$v=1$
0	99164.801	101494.749
1	99228.229	101554.041
2	99354.572	101671.649
3	99542.778	101849.412
4	99791.34	102081.05
5	100098.27	102367.17
6	100461.21	
7	100877.38	
8	· · ·	
9	101857.19	

unresolved components. McIntyre and Hänsch,[20] using Doppler-free saturated absorption, observed regions of the Te_2 spectrum with several transitions per GHz (our full Doppler width is around 1 GHz). This structure sometimes merely broadens the line without markedly altering its Gaussian profile, but in several lines a distinct asymmetry was noted and incorporated as an additional systematic error.

Where an H_2 transition could be recorded with two or more Te_2 reference lines the errors associated with the different Te_2 lines, except those due to interferometer drift, are independent and were treated as random; the error due to interferometer drift was monotonic over several scans and must be treated as systematic.

If the laser and molecular beams do not cross exactly at right angles the resulting Doppler shift will introduce another systematic error. By taking scans with laser beams crossing the molecular beam from opposite sides, overlapped and collinear with each other, we measured this shift and corrected the data accordingly. All measurements of the shift were statistically consistent with 0.

With high pump powers (80 mJ) "chirping" of the laser pulse occurs in the pulsed amplifier and can shift the frequency. To establish an upper limit to the chirp we applied a dc voltage to a spectrum analyzer and tuned it to separately peak the transmission of the cw and pulse amplified lasers. By comparing the peak transmission voltages we estimated the frequency shift to be at most 20 MHz (well below the laser bandwidth).

To determine absolute term energies for the E,F state relative to $X\,^1\Sigma_g^+$, $v=0$, $N=0$, additional data are required because we could not directly measure the (0,0) band. The transition energies from the $v=1$ and 2 levels of the X state can be precisely referenced to the $v=0$ level using the data of Bragg, Brault, and Smith.[1] They measured the first two vibrational spacings for the lowest rotations, with accuracies as high as eight parts in 10^9. Spacings between $v=1$ and $v=2$ levels, $N=0$–3, calculated using combination differences from our data agree with Bragg *et al.* within the stated errors, although there is a suggestion of a slight discrepancy, about 0.01 cm^{-1}. In all four cases our numbers are smaller than those of Bragg *et al.* The (0,0) band of $E,F \leftarrow X$ can also be excited using third-harmonic generation in β-BaB_2O_4. Preliminary new measurements by Glab and Hessler are in agreement with the present results although somewhat less precise.[15]

Table II presents term energies for the E,F state obtained by using the calculated ground-state energies of Schwartz and LeRoy for the rotational intervals,[13] and the measurements of Bragg *et al.* for the vibrational intervals.[1] The lower rotational levels are consistent with those tabulated by Dieke with an overall shift of 8.01(4) cm^{-1}.[21] Using these term energies, the recent preliminary determination of the dissociation energy is unchanged,[7] but the ionization potential reported in Ref. 8 is slightly lowered, to 124417.42 cm^{-1}, and the error bars reduced to ±0.15 cm^{-1}. The two measurements of the ionization potential reported in Ref. 5 are also lowered, to 124417.53 cm^{-1} for the para-H_2 data and 124417.68 cm^{-1} for ortho-H_2 (subtracting the $N=0$ to $N=1$ interval for H_2^+ from the ortho-H_2 result). The large ortho-para discrepancy suggests that the stated errors of 0.03 cm^{-1} for measurements relative to the E,F state are too small.

The accuracy of the current measurements is limited almost entirely by the calibration methods and the rather unstable interferometer used to correct for scan nonlinearities. In the near future an improvement to the level of about 0.003 cm^{-1} can be expected. By obtaining more data on rotational O and S branches and using combination differences, accurate absolute energy levels can be determined for both the X and E,F states. This will be particularly useful for the HD and D_2 isotopes, where accurate theoretical predictions exist but have not been precisely tested.

In conclusion, we have developed a source providing a molecular beam of vibrationally excited ground-state H_2, and used it to determine numerous $E,F \leftarrow X$ intervals to 0.01 cm^{-1}. These measurements can be used to calibrate the absolute energies of higher levels excited by stepwise excitation from the E,F state, and should soon lead to much improved experimental values for the dissociation energy and ionization potential.

This research was supported by the National Science Foundation, Grant No. PHY-8403324. We wish to acknowledge Peter Barnes for his enthusiastic contributions toward developing the discharge source.

[*] Permanent address: Department of Physics, University of Connecticut, Storrs, CT 06268.

[1] S. L. Bragg, J. W. Brault, and W. H. Smith, Astrophys. J. **263**, 999 (1982).

[2] T. E. Sharp, At. Data **2**, 119 (1971).

[3] D. W. Chandler and L. R. Thorne, J. Chem. Phys. **85**, 1733 (1986).

[4] N. Bjerre, R. Kachru, and H. Helm, Phys. Rev. A **31**, 1206 (1985).

[5] W. L. Glab and J. P. Hessler, Phys. Rev. A **35**, 2102 (1987).

[6] D. H. Parker, J. D. Buck, and D. W. Chandler, J. Phys. Chem. **91**, 2035 (1987).

[7] E. McCormack and E. E. Eyler, Bull. Am. Phys. Soc. **32**, 1279 (1987).

[8] E. E. Eyler, R. C. Short, and F. M. Pipkin, Phys. Rev. Lett. **56**, 2602 (1986).

[9] Ch. Jungen and G. Herzberg (unpublished). A brief account of this result is given by P. Senn, P. Quadrelli, K. Dressler, and G. Herzberg, J. Chem. Phys. **85**, 2384 (1986).

[10] G. Herzberg and Ch. Jungen, J. Mol. Spectrosc. **41**, 425 (1972).

[11] G. Herzberg, J. Mol. Spectrosc. **33**, 147 (1970).

[12] G. Herzberg, Comment. Pontif. Acad. Sci. **2**, 1 (1972).

[13] C. Schwartz and R. J. LeRoy, J. Mol. Spectrosc. **420** (1987); W. Kolos and K. Szalewicz, J. Chem. Phys. **84**, 3278 (1986).

[14] I. Dabrowski, Can. J. Phys. **62**, 1639 (1984).

[15] W. L. Glab and J. P. Hessler (private communication).

[16] J. Gilligan and E. E. Eyler (unpublished); see also the Proceedings of the Second International Conference on Laser Science, 1986, Seattle, Washington (to be published).

[17] K. Kato, IEEE J. Quantum Electron. **QE-22**, 1013 (1986).

[18] S. W. Sharpe and P. M. Johnson, J. Chem. Phys. **85**, 4943 (1986).

[19] J. R. Hiskes, A. M. Karo, M. Bacal, A. M. Bruneteau, and W. G. Graham, J. Appl. Phys. **53**, 3469 (1982).

[20] D. H. McIntyre and T. W. Hänsch, Phys. Rev. A **34**, 4504 (1986).

[21] H. M. Crosswhite, *The Hydrogen Molecule Wavelength Tables of Gerhard Heinrich Dieke* (Wiley, New York, 1972).